

### ***Au-Ag-Te-Se deposits***

IGCP Project 486, 2005 Field Workshop, Kiten, Bulgaria, 14-19 September 2005

## **Ore formation at Varatec-Baiut, Baia Mare region, East Carpathians, Romania**

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**Abstract.** The PbZnCu>AuAg ores are located in groups of veins hosted by Tertiary sedimentary and igneous rocks. Sulfides, i.e., pyrite, chalcopyrite, sphalerite and galena, prevail, with subordinate amounts of marcasite, pyrrotite, arsenopyrite, bornite, chalcocite, and covellite. Sulfosalts, i.e., tetrahedrite-tennantite, bournonite, polybasite-peacockite and especially Bi-sulfosalts such as bismuthinite-aikinite, lillianite-gustavite, matildite, pavonite, berryite, and wittichenite, are characteristic of this field. Gold is associated with Bi - inerals, sulfides and gangue minerals. Wolframite, scheelite, hematite and magnetite are also present in the paragenesis. The metallogenesis is polystage, that is Fe±W, Cu Bi±Fe, Pb Zn Cu±Bi, Ba Fe. Metallogenesis of the Varatec-Baiut-Poiana Botizei field is to be assigned to polymetallic > precious metal low sulfur (adularia-sericite) epithermal type / sulfide-rich sub-type.

*Key words:* Varatec-Baiut, Baia Mare District, Romania, epithermal, sulfides, Bi minerals, gold, fluid evolution, magmatic, meteoric fluid

### **Introduction**

The Varatec ore deposit is part of the Baiut – Varatec – Poiana Botizei metallogenetic field, located in the eastern end of the Neogene Baia Mare Metallogenic Province (East Carpathians, Romania). The orebodies have been mined for centuries, providing one of the main economic activities in the region. Previous geological papers focused mainly on the general geology and less on the mineralized structures themselves.

### **Geological setting**

The geology of the area relates to Jurassic, Cretaceous and Paleogene sedimentary formations included in the Pienid units, posttectogenetic Neogene and Quaternary sedimentary

deposits, as well as explosive, effusive and intrusive volcanic sequences. The magmatism associated with ore formation is subduction-related and consists of a volcano-plutonic edifice of calc-alkaline character, mainly andesitic to dioritic in composition. The complex tectonic pattern resulted from the movements leading to the formation of the Pienid Nappes, followed by reactivation of previously-formed faults and the formation of new ones, synchronous with magmatic activity.

The hydrothermal alteration associated with ore-forming processes is potassic and phyllic, locally also propylitic, siliceous and carbonaceous.

### **Description of the ore deposit**

The Văratec ore deposit consists of 18 veins. The Pb-Zn-Cu>Au-Ag veins are hosted by

Tertiary sedimentary and igneous rocks. Three groups can be defined: north-western (Trans-Livia, Livia, Văratec, Radu-Vasile, Gheorghe, Ramură Livia and Maria veins), central (Ioan Vechi, Ioan Nou, Tereza, Alexandru and 200 veins), and south-eastern (350, Botiza II, Botiza I, Botiza III, Botiza IV and Borcut veins) ones.

The veins belong to three fracture systems: NE-SW, ENE-WSW and NNE-SSW. Their length varies between 0.2 and 5.9 km, with an average of 0.9 to 1.5 km. The vein thickness varies between 0.2-0.3 to more than 5.5 m. The current height of the mineralized level is variable, from tens of meters in the case of less-developed veins, up to about 500 m.

The veins show diverse textures, most frequently being present the banded, brecciated, massive, cockade and geode ones; impregnations are subordinate.

### Mineralogical composition

The veins in all the three vein groups of the Văratec ore deposit are almost identical mineralogically, the differences being related to the ratios between the mineral species. The following mineral classes are represented: native elements, sulfides, sulfosalts, wolframates, oxides and hydroxides, carbonates, sulfates and silicates. Among the native elements, gold shows similar compositions throughout the deposit. It can be divided two types of gold: Ag-rich (16.75-18.49 wt.% Ag) and Ag-poor (12.27-15.25 wt.% Ag). Gold is associated with Bi minerals, sulfides and gangue minerals.

Quantitatively, sulfides are dominant: the most frequent species are pyrite, chalcopyrite, sphalerite, and galena. Marcasite, pyrrhotite, arsenopyrite, bornite, chalcocite, and covellite are subordinate. Even if sulfosalts occur in considerably lesser amounts, they nevertheless constitute an essential part of the mineralization. The most frequent sulfosalts are members of the tetrahedrite-tennantite series; bournonite is subordinate, while members of the polybasite-pearceite series occur sporadically. The presence of Bi- sulfosalts is a

characteristic feature of the veins from Văratec. The chemical data showed the presence of members of the bismuthinite-aikinite series, the lillianite-gustavite series, as well as matildite, pavonite, berryite and wittichenite.

Bi-minerals, and especially Bi sulphosalts, all contain Se. The content of Se is up to 2.69 wt.%, the Se-richest minerals being lillianite-gustavite series and berryite.

Another typical mineralogical aspect of Văratec ore deposit is the presence of wolframates. This class is represented by wolframite – the Fe-rich member (ferberite) and scheelite. Among the oxides, hematite and magnetite have been identified, while hydroxides are represented by lepidocrocite and goethite.

Quartz is the most widespread gangue mineral in the Văratec veins. It shows various colors: greyish-white, dark grey or smoky, violet-coloured or transparent. Carbonates are mainly represented by siderite and calcite, rarely by malachite and cerussite. Sulfates are scarce, among which gypsum, barite and rarely anglesite were noticed. Clay minerals occur as nests in the central parts of the veins.

### Mineralogenetic succession

Four distinctive stages may be distinguished within the mineralogenetic processes that led to vein formation. Each is characterized by a specific geochemical assemblage: Fe ± W, Cu – Bi ± Fe, Pb – Zn – Cu ± Bi and Ba – Fe.

The first stage is characterized by the presence of the association quartz – Fe-oxides ± pyrite ± wolframates; it formed close to the wallrock.

For the second stage, the association quartz – chalcopyrite – Bi-minerals – pyrite ± Fe-oxides is typical, including grains of native gold. This association gave birth to the median part of the veins, especially of those belonging to the north-western group.

The third stage represents the main mineralogenetic stage, being characterized by quartz – base metal sulfides ± Bi-minerals. Gold grains are associated with various minerals within this assemblage, which is

located in the central parts of the veins, being more significant in the case of the central and south-eastern groups.

The final stage is characterized by the formation of the quartz-barite-marcasite association, and it formed in the central parts of the veins, especially as geodes.

### **Ore forming conditions**

The study of the hydrothermal solutions was based on fluid inclusions in quartz from all four stages of mineralization. The investigated fluid inclusions are primary, two-phase inclusions, with sizes between 2-3 and 50  $\mu\text{m}$ . The temperature of formation was defined by measuring homogenization temperature, and the salinity of the solution was estimated based on the final ice melting temperature (Potter et al., 1978).

The mineralization took place at temperatures between 228.4-356.6°C, and the salinity of the hydrothermal fluids varied between 0.46 and 3.36 NaCl wt.% equiv. The temperature of formation increases from the first stage till the third stage, when the maximum values were recorded; it then drops again during the fourth stage. The salinity increases from the first stage to the second one which is characterized by the maximum values; it then gradually decreases till the fourth stage.

This evolutionary pattern of the hydrothermal solutions was due to dilution of hot, more saline fluids by colder, less saline fluids (first and fourth stages), as well as to a less significant cooling during the third stage. During the third stage, processes of isothermal mixing of fluids with different salinity and slightly different temperatures overlapped with boiling and dilution with surface fluids (Hedenquist and Henley, 1985; Hedenquist et al., 1992). Most of the density values for the hydrothermal solutions fall within the range 0.7-0.8 g.cm<sup>3</sup> (Wilkinson, 2001).

### **Geochemistry and zoning**

Based on the variation of major element contents with direction, several mineralized

columns can be discriminated in the case of large veins, separated by areas depleted in metals, along several horizons. These columns, showing maximum development in the central parts of the veins, usually disappear at deeper levels. In a vertical profile, the following zones can be separated: an upper Pb-Zn zone enriched in precious metals, a clearly polymetallic, basically Pb-Zn median zone, and a lower, Cu-rich zone. The latter zone also typically shows relatively larger amounts of Au and Ag. The veins in the northwestern group are dominantly Cu-rich, while the veins in the central and south-eastern groups are Pb-Zn-rich.

Based on minor elements, the veins in the north-western and central groups are dominated by W and Bi, while the south-eastern group is characterized by Cd and Sb. Pyrite and marcasite are rich in As, Co, and partly Ni and Ag. Relatively high contents of Ag and Bi were noticed in chalcopyrite, especially in the veins from the north-western group. Galena displays high concentrations of Ag, Bi, and Sb, while sphalerite registers the highest values for Mn and Cd.

### **Metallogensis**

The formation of Văratec deposit was favored by a series of local metallogenetic factors: lithology, tectonics, magmatic features and physical-chemical factors. The specific features of the host rocks influenced the formation and development of the veins, the main role being played by porosity and permeability. The Paleogene deposits and the magmatic rocks represented a favorable geological environment for development of vein fractures, while the volcanoclastic and the Neogene sedimentary deposits were less suitable for this process. The screening effect of Paleogene sedimentary rocks also contributed to the genesis of well-represented mineralized areas.

The tectonic movements affecting the rock sequence in the Văratec Massif led to the formation of fractures that allowed the migration of the hydrothermal solutions. These fractures occurred simultaneously with the

establishment of the regional structural framework, and they were subsequently reactivated during the tectono-magmatic stage. The intersection of several fracture alignments with different orientations represented areas of minimal resistance that favored the emplacement of subvolcanic bodies. Changes of the fractures orientation or dip and their intersection contributed to the enrichment of the mineralizations.

At the initiation of the magmatic activity, the structural framework of Văratec massif was already established, the basement consisting of intensely tectonised Eocene flysch deposits (Fig. 1).

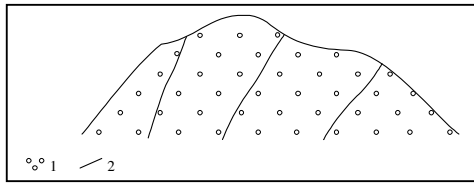


Fig. 1. Deposition and deformation of pre-magmatic basement formation (no scale). Legend: 1 – Paleogene formation, 2 – fractures

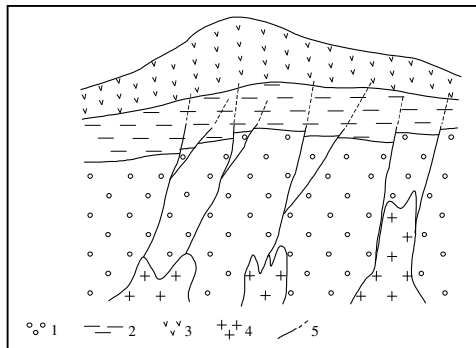


Fig. 2. Development of Neogene magmatic activity (without scale). Legend: 1 – Paleogene formation, 2 – volcanoclastic rocks, 3 – effusive rocks, 4 – subvolcanic bodies, 5 – fractures

The magmatic activity started with an explosive episode that led to the formation of the volcanoclastic complex; an effusive episode followed that produced the lava flows at the upper part of the massif. The intrusive

processes were subsequent to the lava flows, and led to the emplacement of several subvolcanic bodies (Fig. 2). This intrusive sequence played the main role in vein formation, by providing the energy for the convective circulation of the hydrothermal system and some of the components of the hydrothermal solutions (Fig. 3).

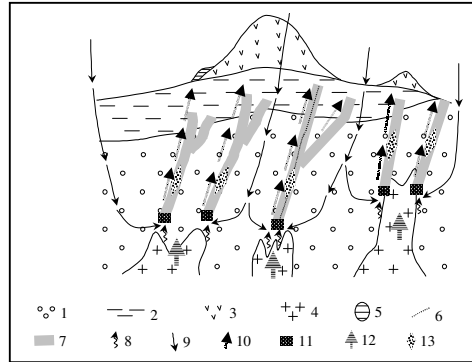


Fig. 3. Formation of the hydrothermal system and mineralizations (no scale). Legend: 1 – Paleogene formations, 2 – volcanoclastic rocks, 3 – effusive rocks, 4 – subvolcanic bodies, 5 – silicified rocks, 6 – vein, 7 – hydrothermal alterations, 8 – magmatic water (CO<sub>2</sub>, SO<sub>2</sub>, HCl), 9 – meteoric water, 10 – hydrothermal solutions, 11 – equilibration with rock, 12 – heat, 13 – boiling

Mineral deposition took place from hydrothermal solutions characterized by a variable thermal regime; the temperature range being over 125°C. The change in the temperatures was connected to the beginning of a new stage. Within the stages rich in metallic minerals (the second and the third stages), several intervals of temperature variation can be noticed during the formation of various mineral associations. The salinity values of the hydrothermal solutions were relatively moderate as compared to the sulfide contents. The high values of salinity are typical for the first three stages, while the deposition of the minerals belonging to the final stage was characterized by lower salinity. The first and the last mineral assemblages were formed from solutions depleted in metallic components. The solutions that led to the formation of the second

mineral assemblage were richer in Cu, while those responsible for the third one had high Pb and Zn contents.

## Conclusions

The geological, tectonic, mineralogical and geochemical characteristics of the Văratec ore deposit define its assignment to the low sulfidation (Hedenquist, 1987), or adularia-sericite (Hayba et al., 1985) epithermal type. Based on the type of metals and associated volcanic rocks, the ore deposit may be considered as rich in polymetallic sulfides associated with andesitic-rhyodacitic rocks (Sillitoe, 1993), or as an intermediate-sulfidation deposit (Hedenquist et al., 2000). All the features of the Văratec ore deposits indicate its best fit with the Creede model (Mosier et al., 1986), while according to the mineralogy, depth and geotectonic setting it belongs to the very low sulfidation subtype (Corbett, 2002). Among the two models previously defined for Baia Mare region (Vlad and Borcos, 1997), the Văratec ore deposit more closely resembles the Baia Sprie model.

The relatively high temperature of formation is due to the genetic relationship with subvolcanic bodies. The wolframite and Bi-mineral signature marks the role played by the magmatic source during ore formation. Furthermore the low salinity suggests involvement of meteoric water, creating a convective system at the Văratec-Baiut magmatic-hydrothermal center.

*Acknowledgment.* The authors are deeply indebted to Dr. Richard Herrington, Dr. Chris Stanley and Dr. Robin Armstrong for their help in performing the analysis and for discussions relating to the subject of this paper. The results are part of the research carried out by D. Costin during a five-month Marie Curie fellowship at Natural History Museum London, U.K.

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